Experimental evidence of chemical-pressure-controlled superconductivity in cuprates

S. Sanna,[1, 2] S. Agrestini,[3] K. Zheng,[2] R. De Renzi,[2] and N. L. Saini[4]

[1]*Dipartimento di Fisica and CNISM, Università di Pavia, Via Bassi 6, 27100 Pavia*
[2]*Dipartimento di Fisica and CNISM, Università di Parma, viale Usberti 7A, 43100 Parma*
[3]*Laboratoire CRISMAT, UMR 6508, ISMRA, Boulevard du Marechal Juin, 14050 Caen, France*
[4]*Dipartimento di Fisica, Università di Roma "La Sapienza", P. le Aldo Moro 2, 00185 Roma, Italy*
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X-ray absorption spectroscopy (XAS) and high resolution X-ray diffraction are combined to study the interplay between electronic and lattice structures in controlling the superconductivity in cuprates with a model charge-compensated $Ca_xLa_{1-x}Ba_{1.75-x}La_{1.25+x}Cu_3O_{6+y}$ ($0 \leq x < 0.5$, $y \approx 7.13$) system. In spite of a large change in T_c, the doped holes, determined by the Cu L and O K XAS, hardly show any variation with the x. On the other hand, the CuO_2 plaquette size shows a systematic change due to different size of substituted cations. The results provide a *direct* evidence for the chemical pressure being a key parameter for controlling the superconducting ground state of the cuprates.

Even after two decades, high T_c superconductivity (HTcS) in cuprates continues to be an area of frontier research in condensed matter physics due to the still unknown mechanism of this quantum matter. It is well established[1] that the transition temperature, T_c, depends on the hole density h, showing a dome shaped behaviour, with a maximum T_c (T_c^{max}) being at an optimum doping ($h^{opt} \sim 0.16$ holes per CuO_2 in each copper plane). However, a debatable question is related to the cause of a significant T_c^{max} variation from one family to the other (from few tens of Kelvin up to a maximum of 135 K) at constant hole density. There is a growing number of experimental evidences[2,3,4,5,6,7,8,9,10,11,12,13,14] that, beyond the hole doping, the CuO_2 plane structure plays an important role, depending on the lattice mismatch with the intercalated layers. This is analogous to what has been known for the manganites[15,16,17,18]; however, the role of the lattice in cuprates is still unclear since, on one hand it is difficult to experimentally separate the lattice effect from that of the hole doping within the same family compound, and on the other hand it is almost impossible to compare different cuprate families, due to the large difference of their structural properties. The charge-compensated compound $Ca_xLa_{1-x}Ba_{1.75-x}La_{1.25+x}Cu_3O_{6+y}$(CLBLCO)[19], offers a rare possibility to explore simultaneously the doping dependence of T_c as well as the origin of the family dependence of T_c^{max}. CLBLCO belongs to the so-called 123 family, but the partial substitution of La on the Ba site hampers the formation of extended $Cu(1)O_y$ chains (e.g. typical of $YBa_2Cu_3O_y$) stabilising the system in a tetragonal phase. In addition, unlike $YBa_2Cu_3O_y$ (YBCO) hole-doping by oxygen loading in CLBLCO spans the complete $T_c(h)$ dome (for $6.9 < y < 7.3$), ranging from the underdoped to the fully overdoped regime. T_c^{max} is achieved at an optimum value of oxygen content[20], $y^{opt} \sim 7.13$. Interestingly, T_c^{max} can be tuned by varying the calcium content, ranging between $0 < x < 0.4$ to shift T_c from 45 K to 80 K.

Here we use the X-ray absorption spectroscopy (XAS), combined with high resolution X-ray diffraction (HRXRD) to address the origin of the variation of T_c^{max} within the model system $Ca_xLa_{1-x}Ba_{1.75-x}La_{1.25+x}Cu_3O_{6+y}$. Firstly we deal with the question whether the variation of T_c^{max} is due to the change of the hole doping in the CuO_2 planes[19,21,22], followed by a study of the CuO_2 in-plane structural modifications. We have performed Cu L (Cu $2p$) and O K-edge (O $1s$) XAS to investigate the electronic structure near the Fermi level, probing unoccupied Cu $3d$ and O $2p$ states (i.e., the hole states), while HRXRD determines any variation in the lattice dimension and order. The results show that the large variation of T_c^{max} with x is not due to the change of the hole density in the CuO_2 planes. On the other hand, there is a systematic variation of the lattice dimension with x, implying that the increase of T_c^{max} should be merely due to changes in the chemical pressure on the CuO_2 sublattice.

The samples used for this work were prepared by the standard solid-state synthesis method[19]. The oxygen was varied by the topotactic technique[23] to drive the samples in the underdoped region and by annealing at 500^oC under an oxygen pressure of $30 - 50$ atm to achieve the optimum T_c^{max}. All the samples were characterized for their phase purity and superconducting properties prior to the XAS and HRXRD measurements. The X-ray absorption spectra were collected at the ISIS beamline of the BESSY storage ring (Berlin, Germany), with energy resolution of ~ 220 meV and ~ 520 meV, respectively at 530 eV and at 930 eV. The measurements were performed at T=20 K by collecting simultaneously the bulk sensitive fluorescence yield signal using a windowless high purity Ge-detector, and the total electron yield by a channeltron detector. The base pressure in the analysis chamber was better than $5 \cdot 10^{-10}$ mbar during the measurements. The samples were scraped in-situ by a diamond file to get clean surfaces. High resolution X-ray diffraction measurements were performed at the beamline ID31 of the ESRF in Grenoble using a wavelength of $\lambda=0.4$ Å.

Fig. 1 displays the Cu L_3-XAS as a function of oxygen (upper) and calcium (bottom) contents. The spectral shape is similar to the one measured on the YBCO
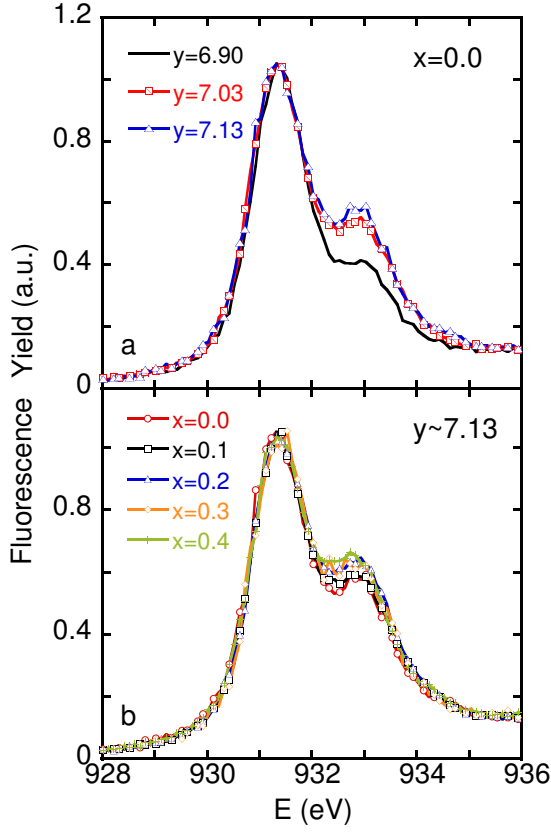
FIG. 1: (Color online) Comparison of the Cu L edge XAS spectra of $Ca_xLa_{1-x}Ba_{1.75-x}La_{1.25+x}Cu_3O_{6+y}$, measured at T=20 K, for various O contents, y, (upper panel) and Ca concentrations, x (lower panel). The introduction of oxygen produces an increase of the intensity of the feature at 933 eV (ligand holes). Negligible variations are observed in the spectra as a function of Ca concentration.

FIG. 2: (Color online) Comparison of the O K edge XAS spectra of $Ca_xLa_{1-x}Ba_{1.75-x}La_{1.25+x}Cu_3O_{6+y}$, measured at T=20 K, for various O contents, y, (upper panel) and Ca concentrations, x, (lower panel). These spectra are normalised with respect to the atomic absorption about 70-80 eV above the absorption jump. Strong variations are evident in the spectra as the oxygen content is changed, while a change of the Ca content does not produce significant modifications. The insets are the zooms over the pre-edge regions (see text).

system[24,25]. Besides a white line at $\sim$931.3 eV representing Cu $3d^9 \rightarrow$ Cu $\underline{2p}\ 3d^{10}$ transition, a shoulder is observed at $\sim$932.8 eV due to Cu $3d^9\underline{L} \rightarrow$ Cu $\underline{2p}\ 3d^{10}\underline{L}$ transition. Here $\underline{L}$ indicates a hole in the oxygen ligand orbital (O $2p$) induced by doping and the intensity of this peak varies proportionally to the density of doping holes (n_h) per Cu site[24,25,26,27]. A clear change in n_h due to the introduction of oxygen in the system is evident in Fig. 1a. Conversely, Fig. 1b shows that Ca concentration (at fixed O content) induces hardly any variation in the ligand hole peak intensity. Unfortunately, since the Cu L_3-XAS spectra are measured on polycrystalline samples, it is hard to distinguish the contributions from chains and planes[24]. Nevertheless, on the basis of the spectra shown in the Fig. 1b, it could be fairly stated that the CLBLCO is globally isoelectronic, consistent with bond valence sum calculations[22].

In order to *selectively* detect the hole doping in the CuO_2 planes we measured the O K-XAS of CLBLCO (Fig.2). The pre-edge region region for all the samples could be easily deconvoluted in three Gaussians of similar width, centered at 527.6 eV, 528.4 eV and 529.5 eV. In
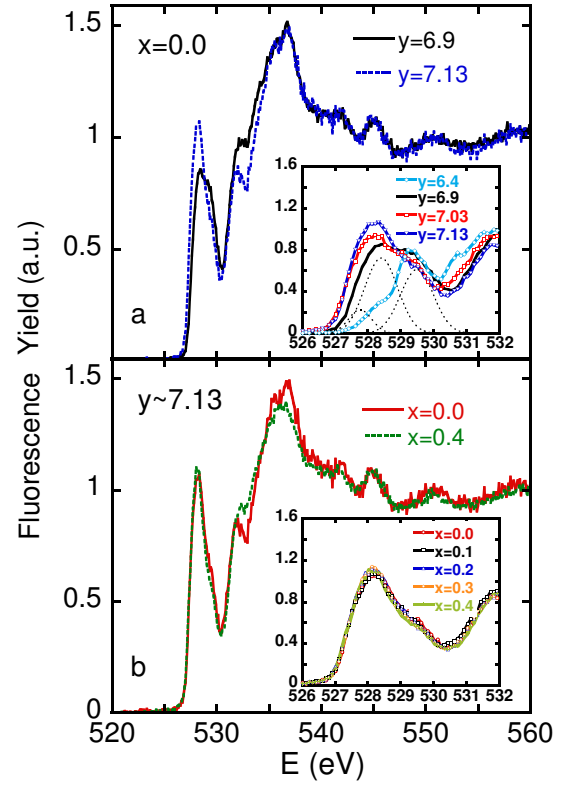
the inset of the upper panel of Fig.2 the dashed curves represent these three peaks for the sample with $x = 0$ and $y = 6.9$. Following the well established peak assignment used for the XAS spectrum of YBCO, these peaks are recognized respectively as : the "chain" plus apical (CA) oxygen, the so-called Zhang-Rice (ZR) singlet and the upper Hubbard band (UHB) contributions[24,25]. As expected, the spectral weights of CA and ZR increase with oxygen, with a corresponding reduction of the UHB signal. In particular the variations of the ZR peak are *directly* related to the change of hole density in the CuO_2 plane[24,25]. On the other hand, if the O content is fixed close to the optimum, with changing Ca the pre-edge region of O K-XAS hardly shows any change (lower panel of the Fig.2). This may be better seen in the inset, which displays the x dependence of the pre-edge region for the CLBLCO samples close to T_c^{max} ($y^{opt} \sim$7.13). It is noteworthy that the shape of the O spectra at low energies, where the CA and the ZR peaks appear, is unchanged by varying x. This is a *direct* experimental evidence that no hole transfer occurs from the chain sites to

the planes. These results are in agreement with previous bond-valence-sum calculations[22] and in contrast to what was supposed in some previous works[19,21].

To further quantify the results, in we have reported the integrated difference $I - I_o$ (proportional to n_h) with respect to the spectrum of a non superconducting composition near the metal-insulator transition (i.e., $LaBa_{1.75}La_{0.25}Cu_3O_{6.9}$) as a function of oxygen (Fig.3a) and calcium (Fig.3b). The integration I was carried out in the energy region 520-528.5 eV and 920-936 eV for the O K and Cu L_3-XAS respectively, and the results are consistent with each other. It can be seen that the introduction of oxygen in the CLBLCO system causes a rise of n_h (Fig. 3a), as expected. On the other hand, a change of Ca concentration does not produce a significant variation (Fig. 3b). Furthermore, we can evaluate the inplane holes, n_{pl}, by considering they are proportional to the intensity of the ZR peak[24,25], $n_{pl} \propto I_{ZR}$, and by the rescaling under the assumption that for the sample close to the metal insulator transitions (y=6.9) is $n_{pl} \approx 0.05$, and at optimum oxygen ($y^{opt} \sim 7.13$) is $n_{pl} \approx 0.16$[1]. The data, displayed in the inset of fig.3b as a function of the Ca content, show that at optimum oxygen n_{pl} is constant within the uncertainties (maximum variation is $\sim$0.02). If we assume that the variation of T_c^{max} from 45 K to 80 K is due to hole doping, for instance by using the parabolic Tallon formula[1], we should expect a change of about 0.07 holes per CuO_2 plane, inconsistent with the present experimental result.

To summarize, the results construct a clear evidence that not only the total number of holes is constant, but also the holes in the CuO2 planes do not change appreciably with x at $y^{opt} \sim 7.13$ in CLBLCO system. Thus it is reasonable to conclude that a large change of T_c^{max} from 45 K to 80 K as a function of x cannot be due to the variation of the in-plane hole density. Therefore, apart from hole density, there should be other parameter which controls the T_c in cuprates. Other responsible parameters could be either substitutional order/disorder and/or the chemical pressure. As far as the former is concerned, it has been revealed that the substitutional disorder does not change or slightly increases[20] with x. Therefore, T_c should be either constant or even reduced[28], inconsistent with the observed behaviour. Thus the increase of T_c with x should be somehow related with the chemical pressure.

Here we should recall that there is a lattice mismatch between the CuO_2 layer and the rock-salt block with a large compressive stress on the CuO_2 plane. This lattice mismatch has been proposed[3,4,5,6] as the third variable needed to define the phase diagram of cuprate perovskites, beyond superconducting temperature T_c and hole doping. In CLBLCO the insertion of calcium cations is accompanied by the substitution of lanthanum at the barium sites which produces an internal mismatch pressure, due to the large difference in ionic radii ($R_{Ca(II)}$=112 pm, $R_{La(III)}$=116 pm, and $R_{Ba(II)}$=142 pm[30]). The variation of this chemical pressure may
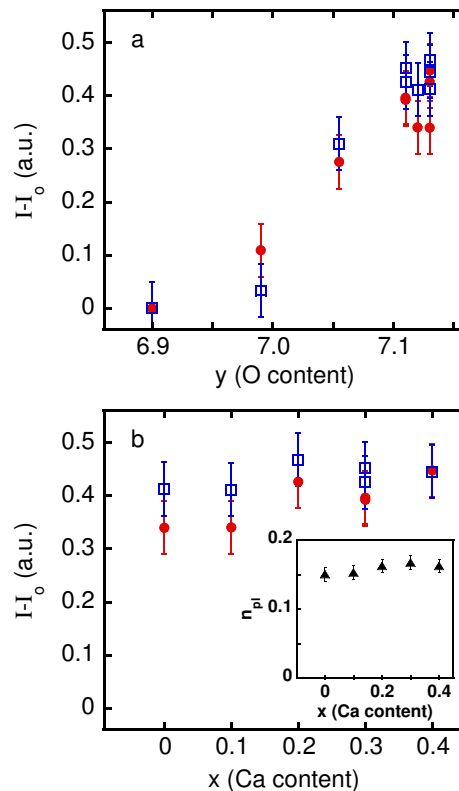

FIG. 3: (Color online) O content, y, (upper panel) and Ca content, x, (lower panel) dependence of the integrated XAS spectral difference (proportional to the hole density per Cu site, n_h), measured at T=20 K. The Cu L-edge (filled circles) and O K-edge (empty squares) XAS spectra of $Ca_xLa_{1-x}Ba_{1.75-x}La_{1.25+x}Cu_3O_{6+y}$ are consistent with each other showing that the hole number increases as oxygen is introduced, while it remains nearly constant as the Ca concentration is varied. The inset (panel b) shows the inplane holes, n_{pl}, proportional to the intensity of the ZR peak, appearing almost constant with x, i.e. no hole transfer takes place from "chain" to planes while T_c^{max} varies from 45 K to 80 K.

be directly determined by measuring the structural parameters (lattice spacing, buckling of the planes, etc.) as a function of x. We have performed a high resolution powder X-ray diffraction (HRXRD) study to measure the effect of Ca doping on the lattice structure. Rietveld analysis did not reveal any structural transition and the atomic parameters are in good agreement with those in the literature[22,31]. In particular, we measured the inplane lattice parameter, a, which is directly linked to the Cu-O distance of the CuO_2 plaquette. Fig.4 shows the evolution of the a-axis for the samples with the T_c^{max} ($y \sim 7.13$) as a function of x (bottom axis), compared with the samples at $x = 0.3$ as a function of the oxygen content y (top axis). The chemical mismatch pressure remains almost constant when the O content is changed, while it shows a substantial variation as a function of x, i.e., when the Ca $\rightarrow$ La $\rightarrow$ Ba substitutions occur. The main effect of the inplane chemical mismatch is the vari-

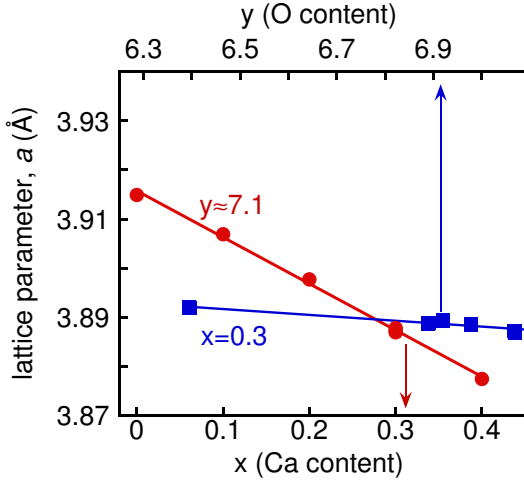FIG. 4: (Color online) In plane lattice parameter a of $Ca_xLa_{1-x}Ba_{1.75-x}La_{1.25+x}Cu_3O_{6+y}$ at $y \sim 7.13$ vs. calcium content (bottom axis), and at $x = 0.3$ vs. oxygen content (top axis). The lattice parameter a, which is directly related with the chemical pressure on the CuO_2 layers, changes as the Ca concentration is modified, while remains nearly constant as oxygen is introduced.
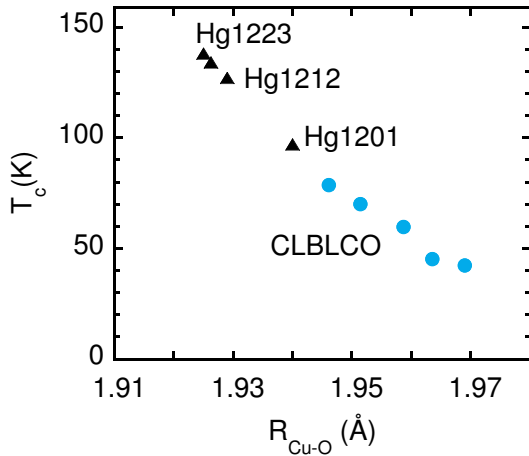

FIG. 5: (Color online) T_c^{max} as a function of the Cu-O inplane distance, $R_{Cu-O} = a/(2cos\theta)$ (where θ is the buckling angle of the CuO_2 planes). The data for the Hg-cuprate family are from Ref.[29].

ation of the Cu-O distance, $R_{Cu-O} = a/(2cos\theta)$. Here θ is the buckling angle of the CuO_2 planes, evaluated by the HRXR diffraction data, and ranges from 5.0(3) to 6.2(3) degrees going from x=0.4 to x=0, in agreement with ref.[31]. Note that this corresponds to a negligible correction to the Cu-O distance (of the order of 0.003 Amstrong). It is well known that the buckling affects the superconducting properties of cuprates[32,33]. However, in CLBLCO the relation between T_c and the buckling angle is complex; with oxygen it increases, while an opposite behavior is observed when the calcium content is varied[31]. In any case it should be considered that the change of T_c as a function of θ for the La_2CuO_4 family

(maximum T_c=45K) is found to be about 3K/Deg (e.g., see fig.3 of Ref.[33]). In the CLBLCO, the change is about 1 Degree from x=0.4 to x=0 that, even renormalizing for the maximum T_c=80K, should lead to a little T_c reduction of about 6K. This is about 6 times smaller than what has been observed, i.e. a change from 80K to 45K. Thus, the variation of the buckling angle cannot explain the T_c changes in the present system as a function of x.

Fig.5 shows T_c^{max} of CLBLCO as a function of R_{Cu-O} following the same trend of the Hg-cuprate family[29] (note that also in this last family the buckling is irrelevant since the CuO_2 planes are flat). The regular scaling of T_c with the Cu-O distance provides clear evidence that the chemical pressure is a key parameter for the superconducting ground state of cuprates. This has been also seen in the new Fe-based superconductors[34]. We do not know what is the intimate mechanism through which the chemical pressure affects the superconductivity, but it can be hypothesized that the chemical pressure tunes somehow the coupling strength among the Cooper pairs.

In summary, we have studied the problem of variation of T_c^{max} using X-ray absorption spectroscopy and high resolution X-ray diffraction on the charge compensated $Ca_xLa_{1-x}Ba_{1.75-x}La_{1.25+x}Cu_3O_{6+y}$ ($0\leq x <0.5$, $y \approx$7.13), a peculiar system that permits to explore independently the effect of two parameters, i.e. the hole density and the chemical pressure. The O K and Cu L_3 XAS provide consistent results with negligible spectral change upon x, suggesting that the large change of T_c^{max} with cationic substitution is not related with the variation of the hole density in the CuO_2 planes. The high resolution X-ray diffraction data reveal a systematic variation in the lattice parameter due to varying the chemical pressure on the CuO_2 sublattice due to cationic substitution in the rock-salt layers of the title system. Since there is a large increase of T_c^{max} with the cationic substitution without any appreciable change in the hole density, the only possibility is that the chemical pressure on the CuO_2 sublattice being the controlling parameter which could act cooperatively with the hole density. Therefore, the results have direct implication on the superconducting ground state of the cuprate perovskites, suggesting that, besides the hole density, the chemical pressure is the second variable that controls the superconducting critical temperature. Although the intimate mechanism which links the chemical pressure to the superconductivity is still unclear, these results provide an important experimental feedback. To further enlighten this problem, CLBLCO single crystals are highly desirable since this compound permits to control T_c at constant doping and within the same cuprate family.

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